

Method of dyeing or printing cellulose-containing fibre materials using disperse dyes

The present invention relates to a method of dyeing cellulose-containing fibre materials, especially fibre blends that contain cellulose, using disperse dyes.

Water-soluble reactive dyes, which produce dyeings having good fastness-to-washing properties, are usually used to dye or print hydrophilic cellulose fibres. In such procedures, the alcoholate groups of the cellulose fibre that are accessible on the surface react with the fibre-reactive groups of the reactive dyes, forming a covalent fibre/dye bond. By contrast, hydrophobic polyester fibres are dyed or printed using water-insoluble disperse dyes, which migrate from the aqueous dye preparation into the hydrophobic fibres. Since the properties of cellulose fibres and polyester fibres are different, the dyeing conditions to be employed will naturally also be different.

An increase in the range of woven and knitted fabrics has resulted in the increased use of natural and synthetic fibres in fibre blends. The usage of natural raw materials, such as cotton, can be considerably reduced by using such blends, while at the same time the quality of the fabrics and their comfort in practical use can also be improved. The increasing use of a very great variety of fibre blends calls for the use of special dyeing procedures that need to take into consideration the properties of each of the fibre components and their behaviour in relation to dyes and accompanying dyeing chemicals.

There are basically two types of method known for dyeing fibre blends: the two-bath method, in which each component of the fibre blend is dyed separately, and the one-bath method, which has only one dyeing operation for all of the fibre components present. The one-bath method is more complicated because, *inter alia*, the conditions need to be matched to the most sensitive of the fibre components, and the dyes chosen for the dyeing frequently have a different affinity for the fibres used. On the other hand, in most cases the one-bath method offers a substantial saving in terms of resources, such as water, energy and the chemicals used.

The need for and the spread, in particular, of fibre blends consisting of cellulose and polyester has grown steadily in recent years.

Fibre blends consisting of cellulose and polyester are usually dyed with a mixture of reactive dyes and disperse dyes, that is to say with at least one suitable dye for each type of fibre. The dyes from the different classes of dye that are to be combined with one another should, in addition to having a comparable affinity for the respective type of fibre, also have identical or at least similar shades, so as to ensure a uniform fabric appearance.

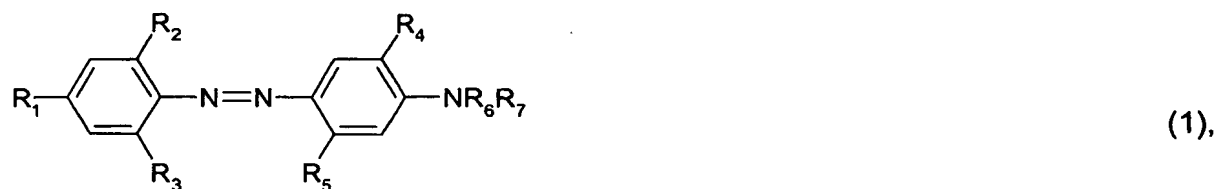
The only suitable method for printing fibre blends consisting of cellulose and polyester is pigment printing, in which a suitable binder resin ensures adhesion of the pigment to the fibre.

There is consequently still a need for a simplified method that is suitable for both dyeing and printing cellulose-containing fibre materials, especially cellulose-containing fibre blends. It should be a one-bath method which dyes the different kinds of fibre simultaneously and produces especially level dyeings or prints that have good allround fastness properties, for example good fastness to light and good wet-fastness.

The present invention accordingly relates to a method of dyeing or printing cellulose-containing fibre materials using disperse dyes that comprises treating the fibre material with an aqueous composition comprising a water-soluble or water-dispersible polyester resin and a water-soluble or water-dispersible acrylate binder.

Suitable disperse dyes for the method according to the invention are those described under "Disperse Dyes" in the Colour Index, 3rd edition (3rd revision 1987 inclusive of Additions and Amendments up to No. 85). Such dyes include, for example, carboxylic acid group-free and/or sulfonic acid group-free nitro, amino, aminoketone, ketoninime, methine, polymethine, diphenylamine, quinoline, benzimidazole, xanthene, oxazine and coumarin dyes and especially anthraquinone and azo dyes, such as mono- or dis-azo dyes.

Preferably, the disperse dyes used in the method according to the invention correspond to formula



wherein

R<sub>1</sub> is halogen, nitro or cyano,

R<sub>2</sub> is hydrogen, halogen, nitro or cyano,

R<sub>3</sub> is hydrogen, halogen or cyano,

R<sub>4</sub> is hydrogen, halogen, C<sub>1</sub>-C<sub>4</sub>alkyl or C<sub>1</sub>-C<sub>4</sub>alkoxy,

R<sub>5</sub> is hydrogen, halogen or C<sub>2</sub>-C<sub>4</sub>alkanoylamino and

R<sub>6</sub> and R<sub>7</sub> are each independently of the other hydrogen, allyl, or C<sub>1</sub>-C<sub>4</sub>alkyl unsubstituted or substituted by hydroxy, cyano, C<sub>1</sub>-C<sub>4</sub>alkoxy, C<sub>1</sub>-C<sub>4</sub>alkoxy-C<sub>1</sub>-C<sub>4</sub>alkoxy, C<sub>2</sub>-C<sub>4</sub>alkanoyloxy, C<sub>1</sub>-C<sub>4</sub>alkoxycarbonyl, phenyl or by phenoxy,



wherein

R<sub>8</sub> is hydrogen, phenyl or phenylsulfonyl, the benzene ring in phenyl and phenylsulfonyl being unsubstituted or substituted by C<sub>1</sub>-C<sub>4</sub>alkyl, sulfo or by C<sub>1</sub>-C<sub>4</sub>alkylsulfonyloxy,

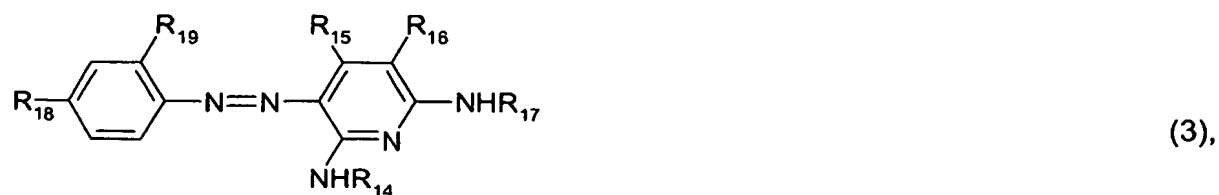
R<sub>9</sub> is unsubstituted or C<sub>1</sub>-C<sub>4</sub>alkyl-substituted amino or is hydroxy,

R<sub>10</sub> is hydrogen or C<sub>1</sub>-C<sub>4</sub>alkoxy,

R<sub>11</sub> is hydrogen, C<sub>1</sub>-C<sub>4</sub>alkoxy, phenoxy or the radical -O-C<sub>6</sub>H<sub>5</sub>-SO<sub>2</sub>-NH-(CH<sub>2</sub>)<sub>3</sub>-O-C<sub>2</sub>H<sub>5</sub>,

R<sub>12</sub> is hydrogen, hydroxy or nitro and

R<sub>13</sub> is hydrogen, hydroxy or nitro,



wherein

$R_{14}$  is  $C_1$ - $C_4$ alkyl unsubstituted or substituted by hydroxy or by phenyl or is phenyl,

$R_{15}$  is  $C_1$ - $C_4$ alkyl,

$R_{16}$  is cyano,

$R_{17}$  is a radical of formula  $-(CH_2)_3-O-(CH_2)_2-O-C_6H_5$ , phenyl, or  $C_1$ - $C_4$ alkyl substituted by hydroxy or by phenyl,

$R_{18}$  is halogen, nitro or cyano and

$R_{19}$  is hydrogen, halogen, nitro, trifluoromethyl or cyano,



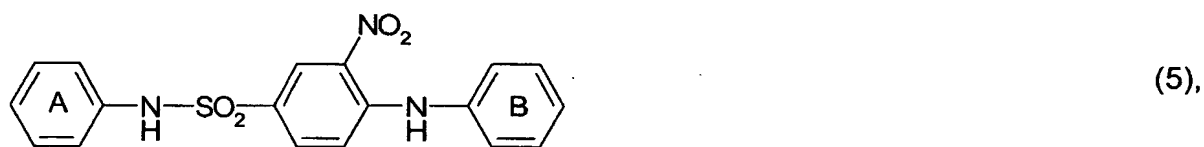
wherein

$R_{20}$  is  $C_1$ - $C_4$ alkyl,

$R_{21}$  is  $C_1$ - $C_4$ alkyl unsubstituted or substituted by  $C_1$ - $C_4$ alkoxy and

$R_{22}$  is the radical  $-COOCH_2CH_2OC_6H_5$  and  $R_{23}$  is hydrogen or

$R_{22}$  is hydrogen and  $R_{23}$  is  $-N=N-C_6H_5$ ,

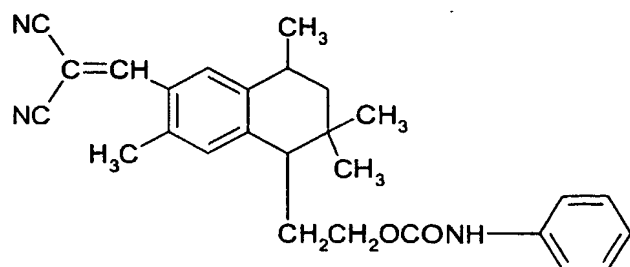


wherein the rings A and B are unsubstituted or mono- or poly-substituted by halogen,

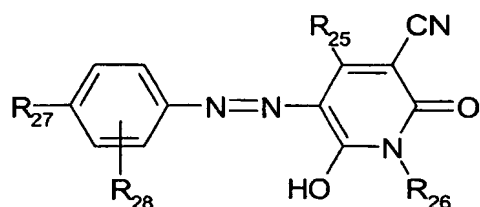


wherein

$R_{24}$  is  $C_1$ - $C_4$ alkyl unsubstituted or substituted by hydroxy,  $C_1$ - $C_4$ alkoxy,  $C_1$ - $C_4$ alkoxy- $C_1$ - $C_4$ alkoxy,  $C_2$ - $C_4$ alkanoyloxy or by  $C_1$ - $C_4$ alkoxycarbonyl,



(7),



(8),

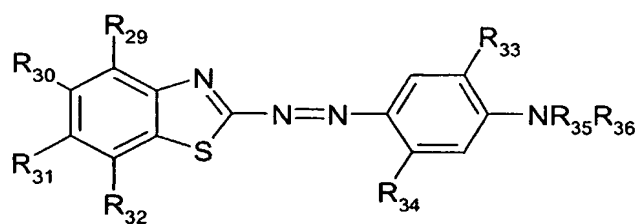
wherein

$R_{25}$  is  $C_1$ - $C_4$ alkyl,

$R_{26}$  is  $C_1$ - $C_4$ alkyl unsubstituted or substituted by  $C_1$ - $C_4$ alkoxy,

$R_{27}$  is hydrogen,  $C_1$ - $C_4$ alkoxy or halogen and

$R_{28}$  is hydrogen, nitro, halogen or phenylsulfonyloxy,



(9),

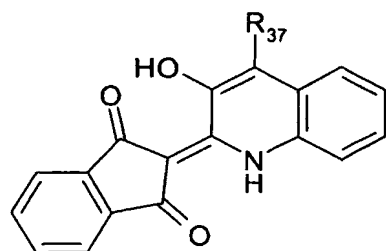
wherein

$R_{29}$ ,  $R_{30}$ ,  $R_{31}$  and  $R_{32}$  are each independently of the others hydrogen or halogen,

$R_{33}$  is hydrogen, halogen,  $C_1$ - $C_4$ alkyl or  $C_1$ - $C_4$ alkoxy,

$R_{34}$  is hydrogen, halogen or acylamino and

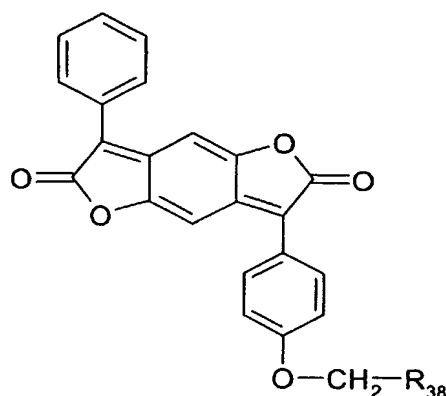
$R_{35}$  and  $R_{36}$  are each independently of the other hydrogen, or  $C_1$ - $C_4$ alkyl unsubstituted or substituted by hydroxy, cyano, acetoxy or by phenoxy,  
or the dye of formula



(10),

wherein

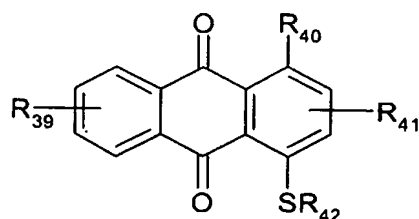
$R_{37}$  is hydrogen or halogen,



(11),

wherein

$R_{38}$  is hydrogen,  $C_1$ - $C_4$ alkyl, tetrahydrofuran-2-yl, or a  $C_1$ - $C_4$ alkoxycarbonyl radical unsubstituted or substituted in the alkyl moiety by  $C_1$ - $C_4$ alkoxy,



(12),

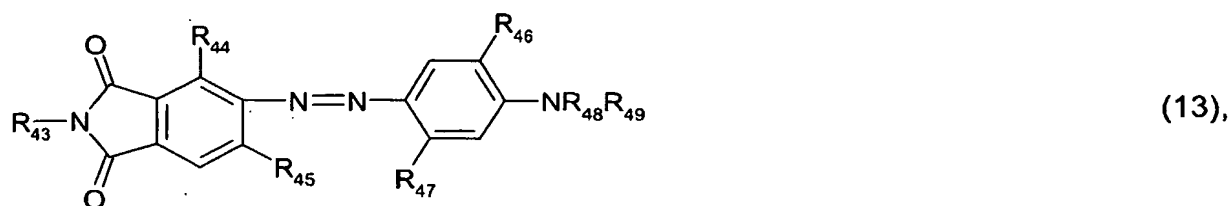
wherein

$R_{39}$  is hydrogen, or thiophenyl unsubstituted or substituted in the phenyl moiety by  $C_1$ - $C_4$ alkyl or by  $C_1$ - $C_4$ alkoxy,

$R_{40}$  is hydrogen, hydroxy, amino, or phenylcarbonylamino wherein the phenyl moiety is unsubstituted or substituted by  $C_1$ - $C_4$ alkyl,

$R_{41}$  is hydrogen, halogen, cyano, or thiophenyl, phenoxy or phenyl each of which is unsubstituted or substituted in the phenyl moiety by  $C_1$ - $C_4$ alkyl or by  $C_1$ - $C_4$ alkoxy and

R<sub>42</sub> is phenyl unsubstituted or substituted in the phenyl moiety by halogen, C<sub>1</sub>-C<sub>4</sub>alkyl or by C<sub>1</sub>-C<sub>4</sub>alkoxy,



wherein

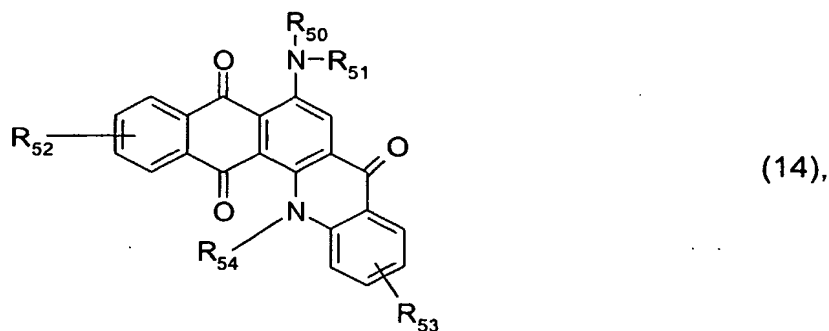
R<sub>43</sub> is hydrogen or C<sub>1</sub>-C<sub>4</sub>alkyl,

R<sub>44</sub> and R<sub>45</sub> are each independently of the other hydrogen, halogen, nitro or cyano,

R<sub>46</sub> is hydrogen, halogen, C<sub>1</sub>-C<sub>4</sub>alkyl or C<sub>1</sub>-C<sub>4</sub>alkoxy,

R<sub>47</sub> is hydrogen, halogen or C<sub>2</sub>-C<sub>4</sub>alkanoylamino and

R<sub>48</sub> and R<sub>49</sub> are each independently of the other hydrogen, or C<sub>1</sub>-C<sub>4</sub>alkyl unsubstituted or substituted by hydroxy, cyano, C<sub>1</sub>-C<sub>4</sub>alkoxy, C<sub>1</sub>-C<sub>4</sub>alkoxy-C<sub>1</sub>-C<sub>4</sub>alkoxy, C<sub>2</sub>-C<sub>4</sub>alkanoyloxy, C<sub>1</sub>-C<sub>4</sub>alkoxycarbonyl, phenyl or by phenoxy, or



wherein

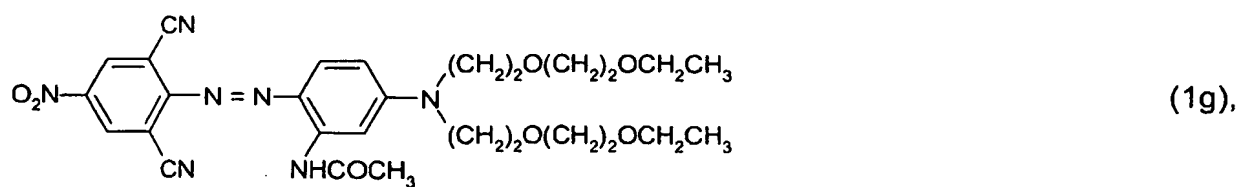
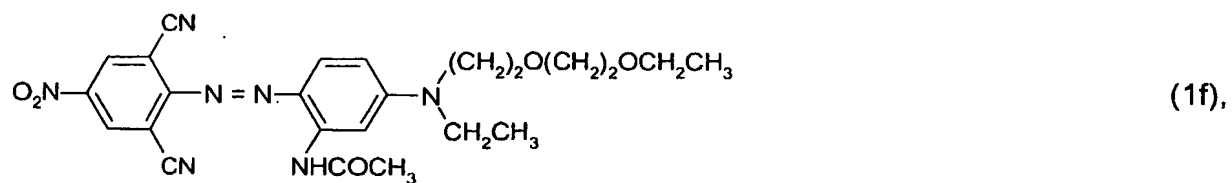
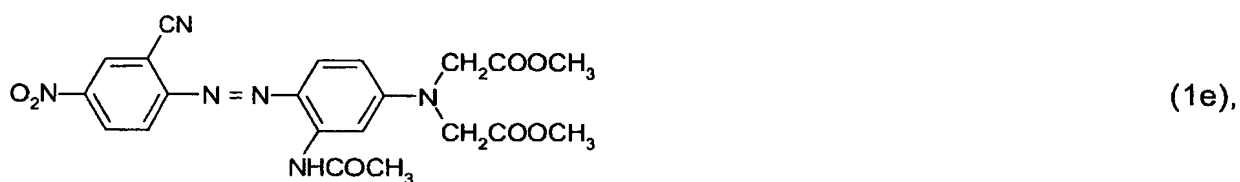
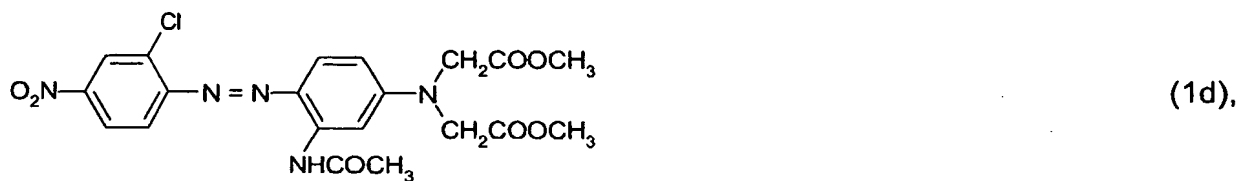
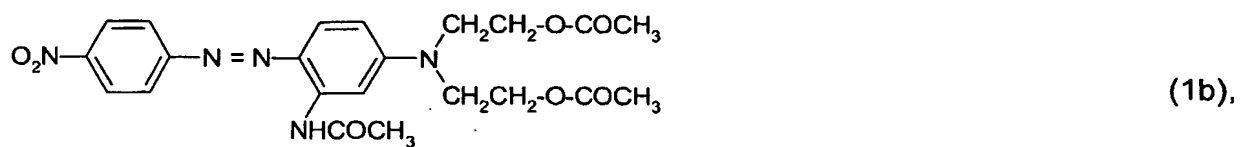
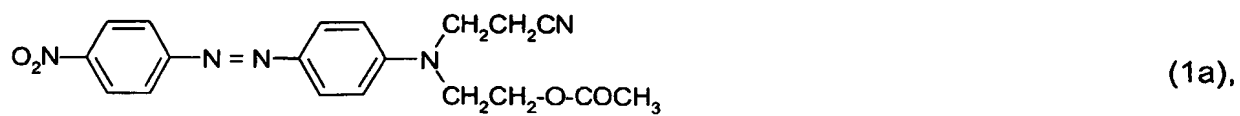
R<sub>50</sub> is hydrogen or C<sub>1</sub>-C<sub>4</sub>alkyl,

R<sub>51</sub> is phenyl or phenylcarbonyl, in each of which the phenyl moiety may be substituted by C<sub>1</sub>-C<sub>4</sub>alkyl,

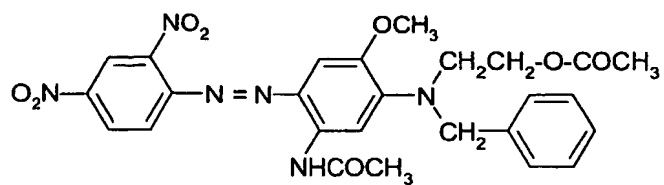
R<sub>52</sub> and R<sub>53</sub> are each independently of the other hydrogen, C<sub>1</sub>-C<sub>4</sub>alkyl or C<sub>1</sub>-C<sub>4</sub>alkoxy and

R<sub>54</sub> is hydrogen or C<sub>1</sub>-C<sub>4</sub>alkyl.

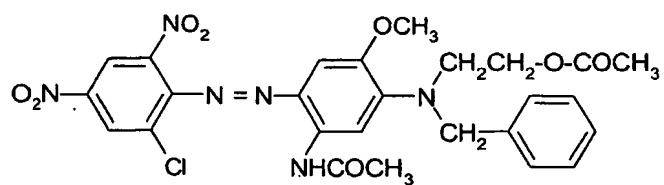
Examples of the disperse dyes used in the method according to the invention that may be mentioned include the dyes of formulae



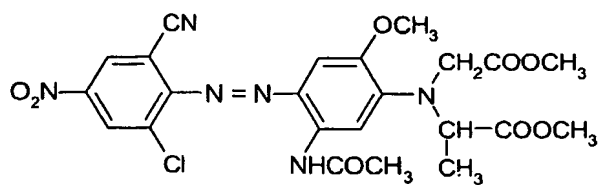




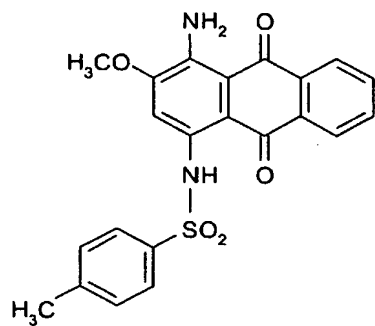
(1i),



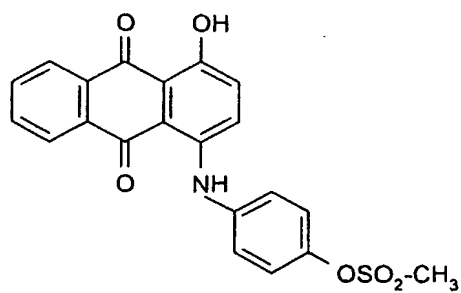
(1j),



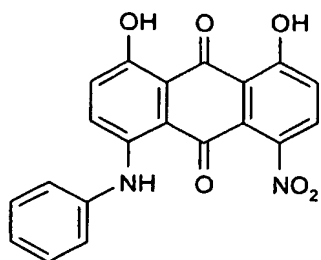
(1k),



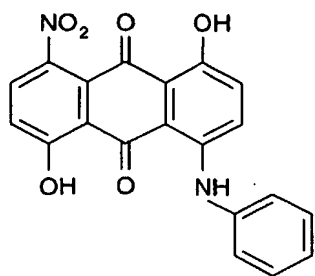
(2a),



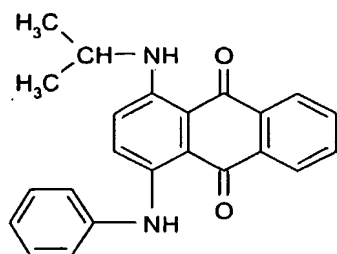
(2b),



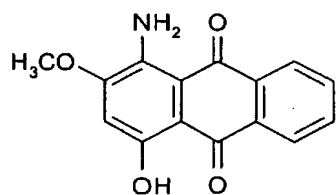
(2c),



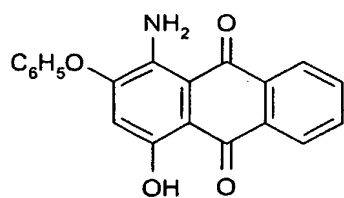
(2d),



(2e),



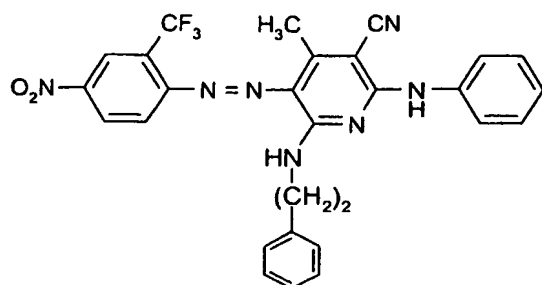
(2f),



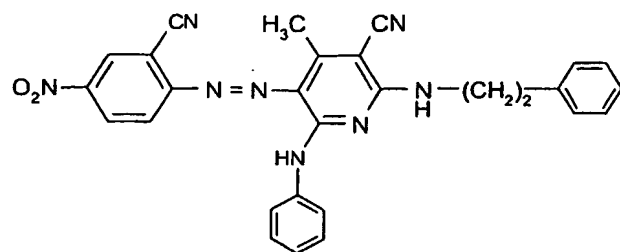
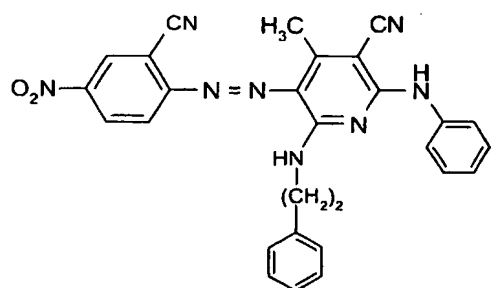
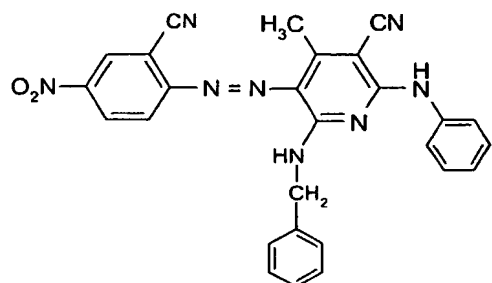
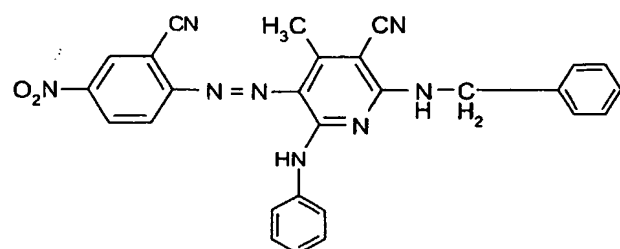
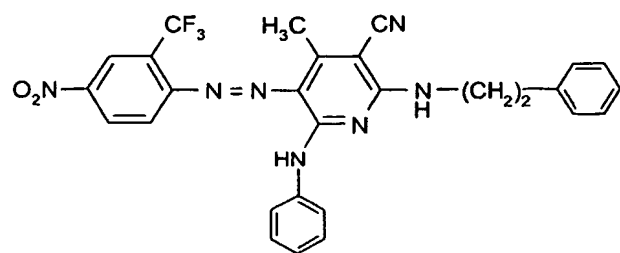
(2g),

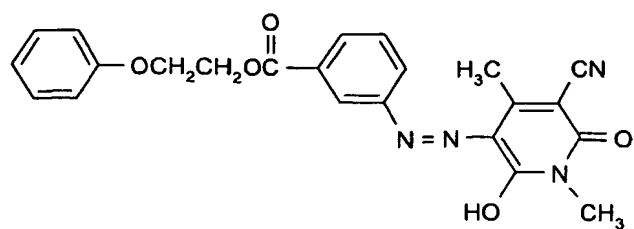


(3a),

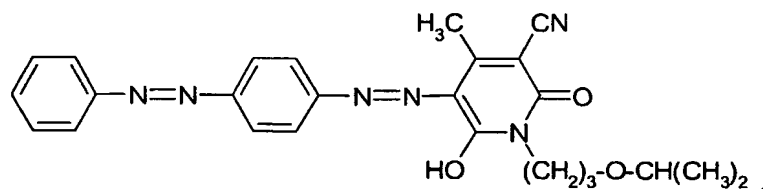


(3b),

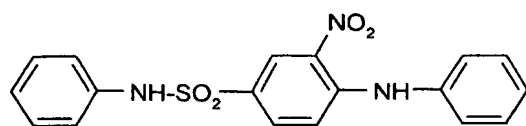




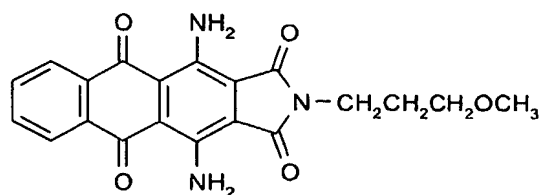
(4a),



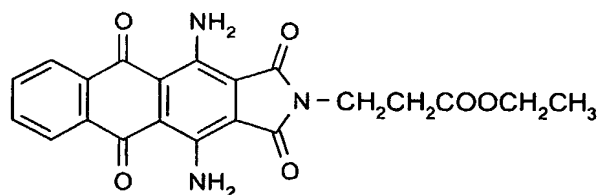
(4b),



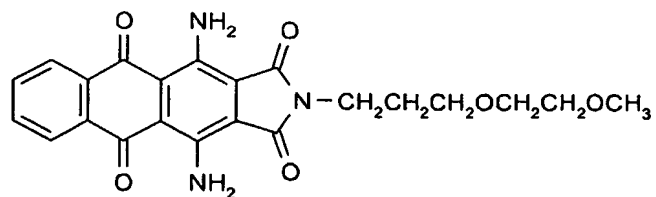
(5a),



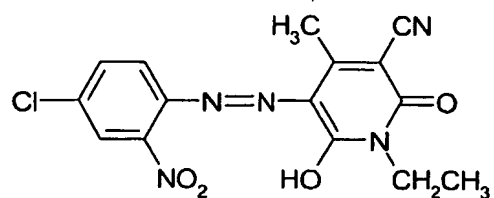
(6a),



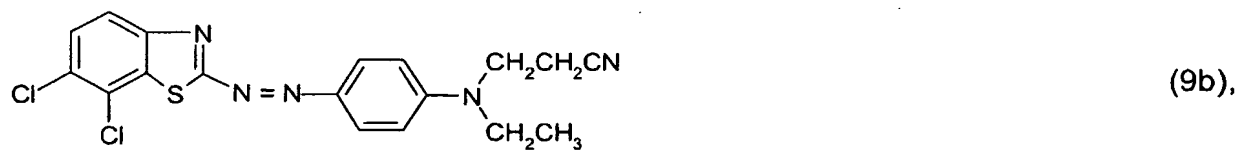
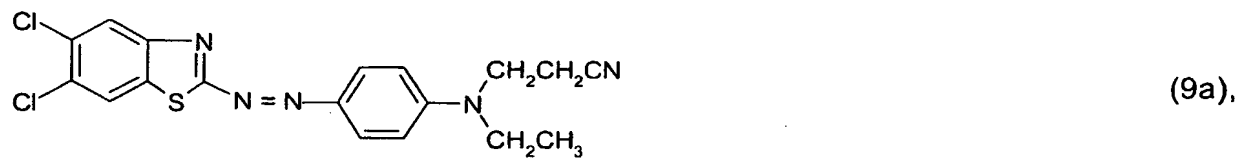
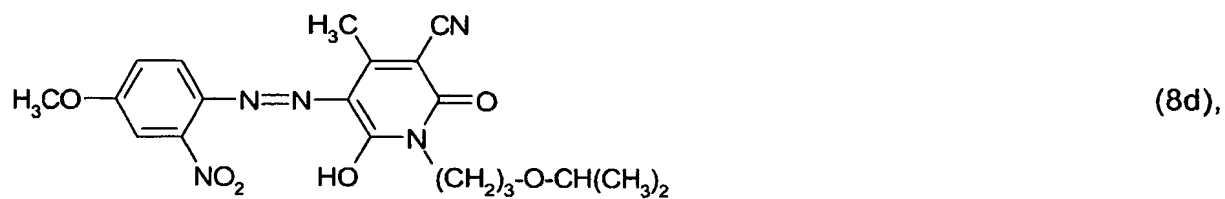
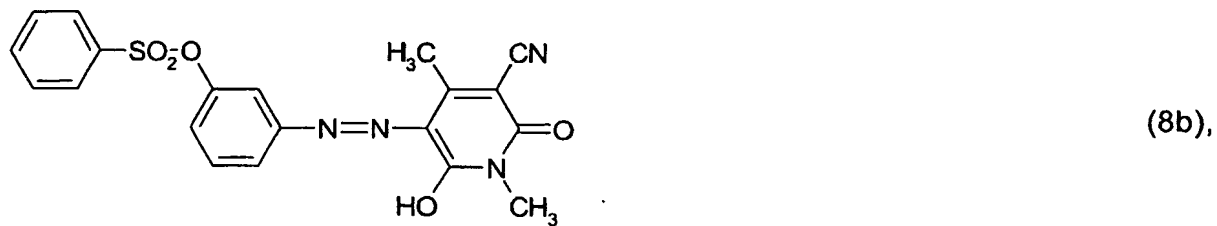
(6b),

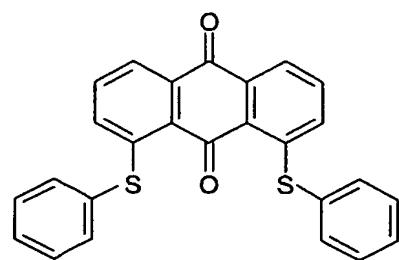
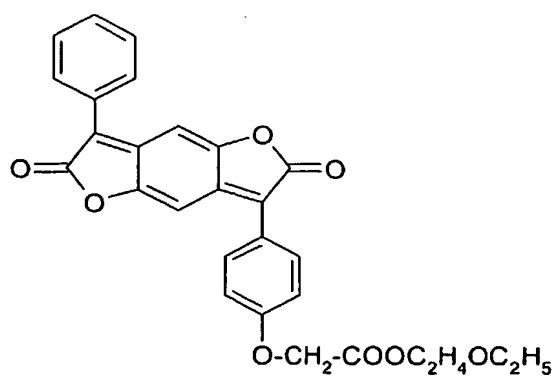
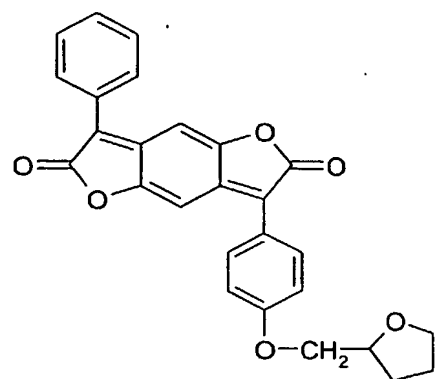
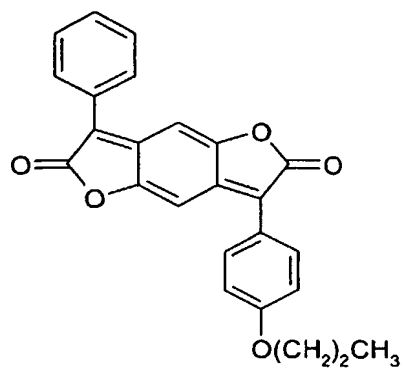


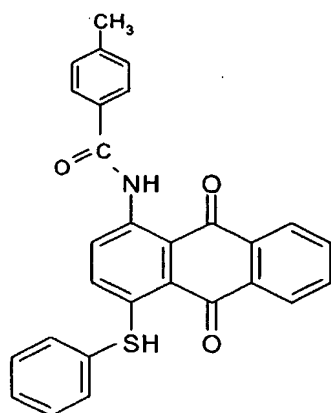
(6c),



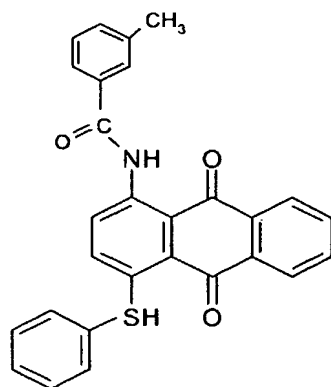
(8a),



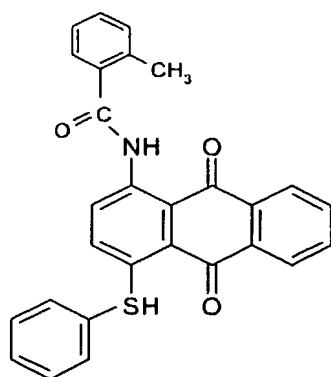




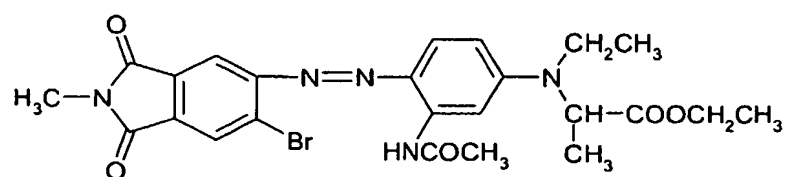
(12b),



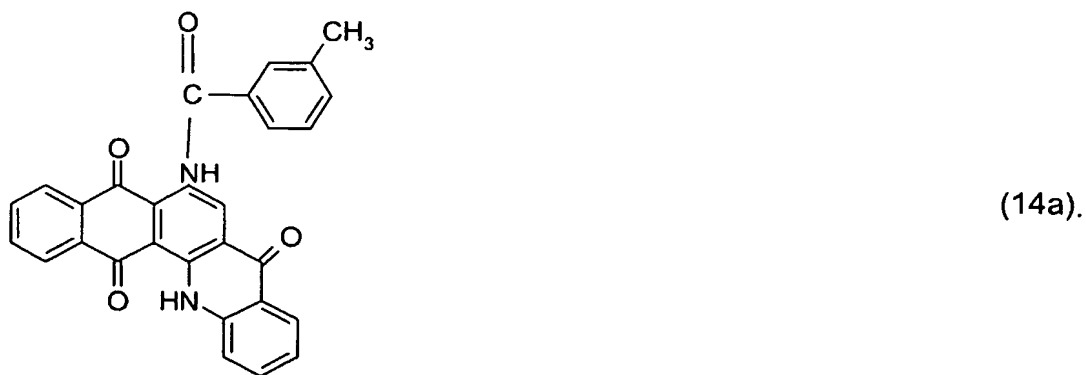
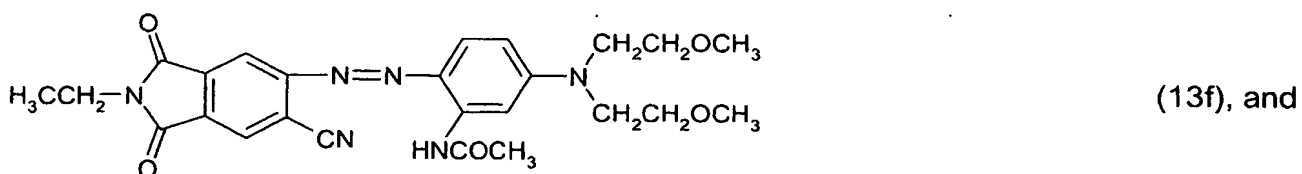
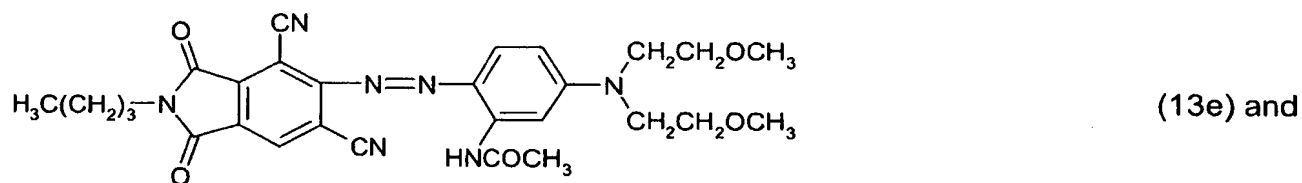
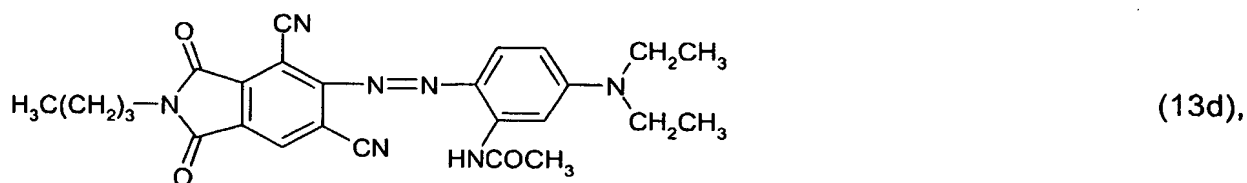
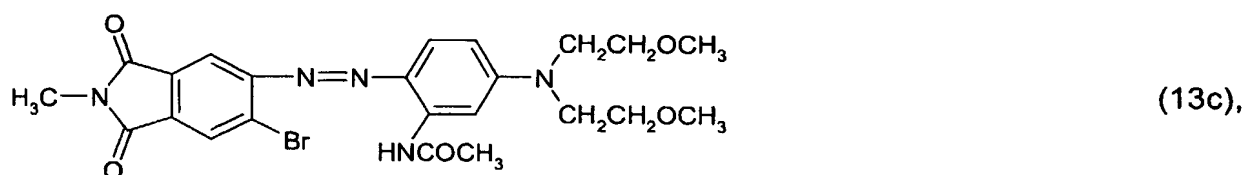
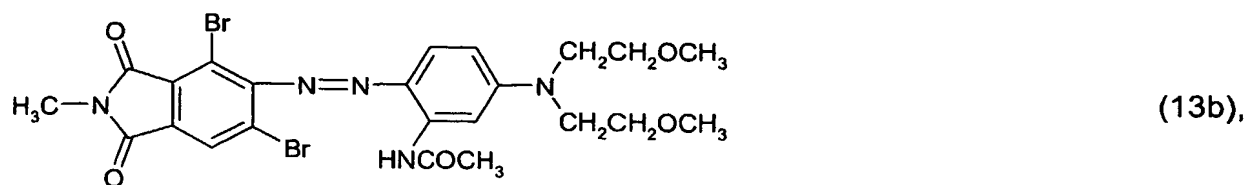
(12c),



(12d),



(13a),



The disperse dyes employed in the method according to the invention can be used on their own or in the form of a mixture of two or more disperse dyes.



Preference is given to disperse dyes of formulae (1), (3), (4), (6), (8), (11), (12), (13) and (14), especially the disperse dyes of formulae (3), (6), (8), (12), (13) and (14).

Very special preference is given to the disperse dyes of formulae (3b), (3c), (3d), (3e), (3f), (3g), (6a), (6c), (8c), (8d), (12a), (12b), (12c), (12d), (13b), (13d), (13e) and (14a).

Special preference is given likewise to the disperse dyes of formulae (1d), (1e), (1f), (1g), (1h), (1i), (1j), (1k), (4a), (6b), (8a), (8b), (8c), (8d), (11b), (13a), (13b), (13c), (13d), (13e) and (13f).

The disperse dyes of formulae (1) to (14) are known or can be prepared analogously to known compounds according to standard procedures, for example by customary diazotization, coupling, addition and condensation reactions.

Suitable acrylate binders are the binders known from textile pigment printing and they include, for example, acrylic polymers, for example poly(meth)acrylates and mixed polymers of (meth)acrylates with suitable comonomers, for example acrylic acid, methacrylic acid, maleic acid, fumaric acid, itaconic acid, mesaconic acid, citraconic acid, vinylacetic acid, vinyloxyacetic acid, vinylpropionic acid, crotonic acid, aconitic acid, allylacetic acid, allyloxyacetic acid, allylmalonic acid, 2-acrylamido-2-methylpropanesulfonic acid, glutaconic acid or allylsuccinic acid, or with esters of such acids, (meth)acrylamide, N-vinylpyrrolidone, N-vinylformamide, N-vinylacetamide, (meth)acrolein, N-vinyl-N-methylacetamide, vinylcaprolactam, styrene derivatives or vinylphosphonic acid; polyamide derivatives; synthetic resin dispersions; vinyl-based mixed polymers; diamide/aldehyde precondensation products; mixed polymers containing N-vinyl lactam, and butadiene-based polymers. Suitable acrylate binders are soluble in aqueous medium or soluble in aqueous medium containing water-miscible organic solvents, if necessary with the addition of bases. The said acrylate binders are preferably used in the form of an aqueous formulation. Such acrylate binders are available commercially in acid form or in partially or fully neutralised form, e.g. Primal® (Rohm & Haas), Neocryl® (NeoResins), Carbocet® (BF Goodrich), Joncryl® (Johnson Polymers) or ALCOPRINT® (Ciba Spezialitätenchemie) binders.

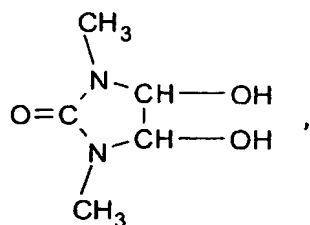
Suitable water-soluble or water-dilutable/water-dispersible polyester resins are known from the coatings industry in which they are used as binders in the preparation of environmentally

friendly, water-based paints. Such polyester resins are described, for example, in US-A-4 054 614. They are preferably used in the form of an aqueous formulation and are available commercially, e.g. Dynapol® (Degussa), Bayhydrol® (Bayer) or Worlée®Pol (Worlée) resins.

The ratio by weight of polyester resin to acrylate binder in the composition (in the form of a dry mass) is, e.g., from 4:1 to 1:1, preferably from 2:1 to 1:1.

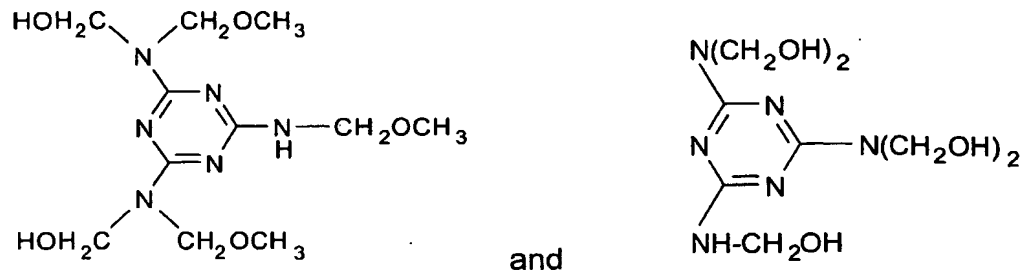
It is also possible, in addition, to use crosslinking agents that react with the hydroxyl groups of the acrylate binder and polyester resin. Such crosslinking agents can be applied to the fibre material simultaneously with or before or after the acrylate binder and polyester resin. Preferably, they are additionally present in the aqueous compositions used in accordance with the invention and are applied to the fibre material simultaneously with the acrylate binder and the polyester resin.

Suitable crosslinking agents include, for example, water-soluble melamine, formaldehyde-melamine, and formaldehyde-urea resins or precondensation products, such as trimethylolmelamine, hexamethylolmelamine or dimethylolurea or water-soluble formaldehyde (pre)condensation products with formamide, thiourea, guanidine, cyanamide, dicyandiamide and/or water-soluble organic sulfonates, e.g. naphthalenesulfonic acid sodium salt, or glyoxalic urea derivatives, e.g. the compound of formula



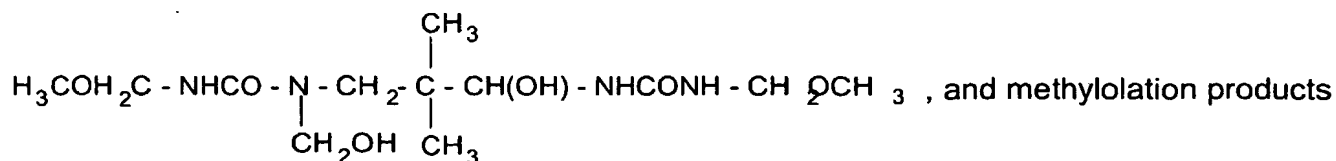
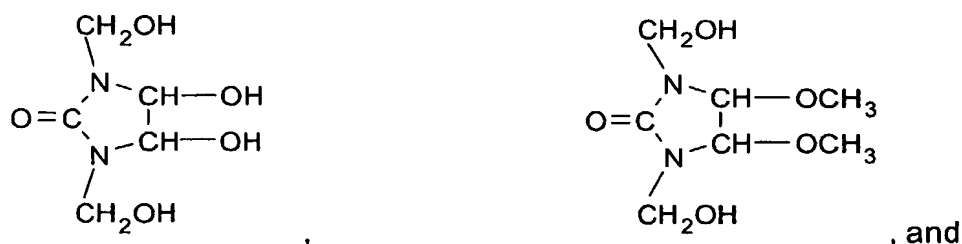
and especially N-methylol derivatives of nitrogen-containing compounds, e.g. non-etherified or etherified melamine-formaldehyde condensation products or N-methylolurea compounds.

The compounds of formulae



are examples of non-etherified or etherified melamine-formaldehyde condensation products. The non-etherified or etherified N-methylolurea compounds are, for example, non-etherified or subsequently etherified reaction products of formaldehyde with urea or urea derivatives, examples of suitable urea derivatives being cyclic ethylene- or propylene-ureas, which may also contain substituents such as hydroxyl groups in the alkylene group, urones and unsubstituted or substituted triazone resins.

Examples of such N-methylolurea compounds include unmodified and modified N-methylol-hydroxyethyleneurea products, for example the compounds of formula



based on propyleneurea or ethyleneurea-melamine.

Crosslinking agents to which preference is given include unmodified and modified N-methylol-hydroxyethyleneurea compounds, methylation products based on propyleneurea or ethyleneurea-melamine and especially non-etherified or etherified melamine-formaldehyde condensation products. It is also possible to use mixtures of two or more different water-soluble crosslinking agents, for example a mixture consisting of a non-etherified melamine-formaldehyde condensation product and an only partially etherified melamine-formaldehyde condensation product.

Suitable crosslinking agents are known commercially, for example under the name ALCOPRINT® (Ciba Spezialitätenchemie).

If desired, crosslinking catalysts can be used in addition.

Crosslinking catalysts suitable for the method according to the invention include, e.g., any agents customarily used as catalysts for imparting anti-crease and anti-shrink properties, such as are known from the *Textilhilfsmittelkatalog* 1991, Konradin Verlag R. Kohlhammer, Leinfelden-Echterdingen 1991. Examples of suitable crosslinking catalysts include inorganic acids, e.g. phosphoric acid; Lewis acids, e.g. zinc chloride, zirconium oxychloride,  $\text{NaBF}_4$ ,  $\text{AlCl}_3$ ,  $\text{MgCl}_2$ ; ammonium salts, e.g. ammonium sulfate, ammonium chloride; and hydrohalides, especially hydrochlorides of organic amines, e.g.  $\text{CH}_3\text{-CH}_2\text{-CH}_2\text{-NH-CH}_3 \cdot \text{HCl}$ . Preference is given to the use of ammonium salts or magnesium-containing Lewis acids and especially to the use of ammonium chloride or magnesium chloride.

In order to increase the softness of the dyed or printed fibre material and thus obtain a certain handle, the aqueous compositions used in accordance with the invention may additionally comprise an agent imparting soft-handle properties. Soft-handle agents are known in the textile industry. They are non-ionic, anionic, cationic or amphoteric softeners. Emulsions of silicones, usually high-molecular-weight  $\alpha,\omega$ -dimethylpolysiloxane, are especially important. Soft-handle agents based on silicone emulsions are preferred. Such soft-handle agents are known commercially, for example under the name ULTRATEX® (Ciba Spezialitätenchemie AG).

The cellulose-containing fibre materials are preferably fibre blends that contain cellulose, e.g. cellulose/polyester or cellulose/polyamide fibre blends, especially cellulose/polyester fibre blends.

The fibre materials can be in a very great variety of processing forms, e.g. in the form of fibres, filaments, yarn, scrap material, woven fabric or knitted fabric, preferably woven fabric or knitted fabric.

The treatment of the fibre material with the aqueous composition can be carried out before or simultaneously with the dyeing or printing step. When the treatment and dyeing are carried out simultaneously, the dyeing composition, for example the dye liquor or printing paste, additionally contains the above-mentioned components, such as acrylate binder and polyester resin, present in the aqueous composition. Preference is given to carrying out the treatment with the aqueous composition before the material is brought into contact with the disperse dye, as a pretreatment prior to the actual dyeing or printing step. A further preferred embodiment comprises, in addition to the first treatment which is carried out prior to or simultaneously with the dyeing or printing step, a further treatment with the aqueous composition, which is a finishing treatment carried out following the dyeing or printing step. Advantageously, with that aftertreatment, any washing and rinsing steps can be avoided.

The pretreatment liquor, like the aftertreatment liquor, can be applied to the fibre material in a variety of ways, for example according to the exhaust method and preferably by the pad-dyeing method.

When the treatment with the aqueous composition is carried out as a pretreatment, prior to the dyeing or printing step, the fibre material impregnated with the pretreatment liquor is advantageously subjected to a drying step, for example for from 0.5 to 10 minutes at from 80 to 140°C, especially for from 1 to 4 minutes at from 100 to 120°C, and then the condensation of the polymer matrix applied to the fibres is carried out, for example, for from 0.5 to 10 minutes at from 140 to 210°C, especially for from 0.5 to 4 minutes at from 150 to 180°C.

When an aftertreatment with the aqueous composition is optionally carried out following the dyeing or printing step, the fibre material impregnated with the aftertreatment liquor is advantageously subjected to a drying step, for example for from 0.5 to 10 minutes at from 80 to 140°C, especially for from 1 to 4 minutes at from 100 to 120°C, and then the condensation of the polymer matrix applied to the fibres is carried out, for example, for from 0.5 to 10 minutes at from 140 to 210°C, especially for from 0.5 to 4 minutes at from 150 to 180°C.

The aqueous composition used in accordance with the invention contains the above-mentioned components (as a dry mass) for example in the amounts indicated below based on the weight of the treatment liquor :

acrylate binder:	from 2 to 20% by weight, preferably from 5 to 20% by weight
polyester resin:	from 2 to 20% by weight, preferably from 5 to 20% by weight
crosslinking agent:	from 0 to 5% by weight
softener:	from 0 to 10% by weight

The cellulose-containing fibre materials can be dyed with the disperse dyes according to customary methods known for dyeing polyester fibres, for example according to the thermosol method, the exhaust method or continuous method. The exhaust method is preferred. The liquor ratio depends on the parameters of the apparatus, the substrate and the form of presentation, but can be selected from within a wide range, for example within a range of from 1:4 to 1:100; preferably it is within a range of from 1:6 to 1:25.

It is advantageous to convert the disperse dyes employed into a dye preparation before use. For that purpose, the dye is ground so that its average particle size is from 0.1 to 10 microns. The grinding can be carried out in the presence of dispersing agents. For example, the dried dye is ground with a dispersing agent, or is kneaded into paste form with a dispersing agent and then dried *in vacuo* or by atomising. The resulting preparations can be used to prepare printing pastes and dye baths after the addition of water.

In the case of printing, the customary thickeners will be employed, e.g. modified or non-modified natural products, for example alginates, British gum, gum arabic, crystal gum, locust bean flour, tragacanth, carboxymethyl cellulose, hydroxyethyl cellulose, starch or synthetic products, for example polyacrylamides, polyacrylic acid or copolymers thereof, or polyvinyl alcohols.

Printing can also be carried out according to the inkjet printing method. In the past years there has been a significant increase in importance in the use of inkjet printing methods for the production of printed textile materials. Such a method involves individual droplets of ink being sprayed onto the substrate in a controlled manner from a nozzle. For that purpose, mainly the continuous inkjet method and the drop-on-demand method are used. In the continuous inkjet method the droplets are produced continuously, the droplets not required for the printing operation being discharged into a receptacle and usually recycled. In the drop-on-demand method, however, the droplets are produced and used for printing as required, that is to say, droplets are produced only when necessary for the printing operation.

The droplets can advantageously be produced, for example, by means of a piezo inkjet head or by means of thermal energy (the so-called bubble jet). For the method according to the invention, preference is given to printing according to the continuous inkjet method or the drop-on-demand method. The preparation of the necessary disperse dye inks and the printing method procedure are described, for example, in US-A-6 284 004.

In addition to comprising the components indicated above, the pretreatment liquor or the dye composition may comprise further components, e.g. stabilisers, such as UV absorbers, light stabilisers, antioxidants etc..

The treatment according to the invention renders the cellulose fibres dyeable by disperse dyes. Dyeing and printing methods for fibre blends are consequently substantially simplified. It is thus possible for all components of the fibre blends to be dyed simultaneously using dyes from one class of dyes (disperse dyes), that is to say, in addition to the polyester component of a cellulose/polyester fibre mixture being dyed, the cellulose component will also be dyed without any problem using the same dye.

The method according to the invention furthermore meets the important requirement that, when it is used for fibre blends, the dyeability of the polyester component is fully retained. In addition, the matrix of acrylate binder and polyester resin applied to the fibres survives, undamaged, the conditions of a conventional high-temperature dyeing procedure for polyester, e.g. 30 minutes at 130°C.

The dyeings or prints obtained using the method according to the invention have very good fastness to light and good wet-fastness properties, such as fastness to washing, to water, to seawater, to cross-dyeing and to perspiration. Also, level dyeings with respect to the fibres and the areas dyed are obtained.

The following Examples are intended to illustrate the invention without limiting the invention to the Examples specifically given.

Example 1:

a) A woven textile fabric consisting of 100% bleached cotton is pad-dyed with an aqueous liquor (liquor pick-up 70%) containing the following additives, each in the form of an aqueous formulation in the amounts indicated:

- 100 g/l of acrylate binder (ALCOPRINT® PB-HC),
- 10 g/l of methylol-melamine crosslinking resin (ALCOPRINT® PFL),
- 50 g/l of wash-fast softener (ULTRATEX® FSA),
- 100 g/l of water-soluble polyester resin (Worlée® Pol 192)

The impregnated fabric is then dried for 2 minutes at 120°C and the applied polymer matrix is condensed for a further 2 minutes at 180°C.

b) 10 g of the fabric pretreated according to a) are introduced into 100 ml of a dye liquor containing

- 0.1 g of the disperse dye of formula (4b),
- 0.1 g of dispersing agent (UNIVADIN® DP),
- 0.1 g of deaerating agent (ALBEGAL® FFD) and
- 0.1 g of ammonium sulfate,

adjusted to pH 4.5 using dilute acetic acid, and heated to 130°C in a pressure vessel. After 30 minutes at 130°C, the liquor is cooled, and the dyed goods are removed, cold-rinsed, washed off for 15 minutes at 95°C in the presence of a wetting agent, rinsed again, dried, and finished by dry heat fixing (30 seconds at 180°C).

An orange dyeing exhibiting a high degree of levelness and good allround fastness properties is obtained.

Example 2:

By proceeding as described in Example 1 but using, instead of a woven cotton fabric, a woven fabric consisting of a 50% cotton/50% polyester fibre blend, there is likewise obtained an orange dyeing that exhibits a high degree of levelness and good allround fastness properties.



**Example 3:**

A woven textile fabric consisting of 100% bleached cotton is pad-dyed with an aqueous liquor (liquor pick-up 70%) containing the following additives, each in the form of an aqueous formulation in the amounts indicated:

- 100 g/l of acrylate binder (ALCOPRINT® PB-HC),
- 10 g/l of methylol-melamine crosslinking resin (ALCOPRINT® PFL),
- 100 g/l of water-soluble polyester resin (Worlée® Pol 192)
- 14.3 g/l of dye formulation, containing 43% by weight of a finely ground active substance of formula (4b).

The impregnated fabric is then dried for 2 minutes at 120°C and the applied polymer matrix is condensed for a further 2 minutes at 180°C, then cold-rinsed, washed off for 5 minutes at 95°C and rinsed again. A level orange cotton dyeing exhibiting a high degree of fastness to light and good fastness to water and to rubbing is obtained.

**Example 4:**

By proceeding as described in Example 3 but using, instead of a woven cotton fabric, a woven fabric consisting of a 50% cotton/50% polyester fibre blend, there is likewise obtained an orange dyeing that exhibits a high degree of levelness and good allround fastness properties.

**Example 5:**

A woven textile fabric consisting of 100% bleached cotton is pad-dyed with an aqueous liquor (liquor pick-up 70%) containing the following additives, each in the form of an aqueous formulation in the amounts indicated:

- 100 g/l of acrylate binder (ALCOPRINT® PB-HC),
- 10 g/l of methylol-melamine crosslinking resin (ALCOPRINT® PFL),
- 100 g/l of water-soluble polyester resin (Worlée® Pol 192)
- 14.3g/l of dye formulation containing 43% by weight of a finely ground active substance of formula (12a).

The impregnated fabric is then dried for 2 minutes at 120°C and the applied polymer matrix is condensed for a further 2 minutes at 200°C. The fabric is then pad-dyed with an aqueous liquor (liquor pick-up 70%) containing the following additives, each in the form of an aqueous formulation in the amounts indicated:

100 g/l of acrylate binder (ALCOPRINT® PB-HC),  
20 g/l of methylo-melamine crosslinking resin (ALCOPRINT® PFL),  
100 g/l of water-soluble polyester resin (Worlée® Pol 192).

The impregnated fabric is then dried for 2 minutes at 120°C and the applied polymer matrix is condensed for a further 2 minutes at 200°C, yielding, without further washing and rinsing steps, a level yellow cotton dyeing that exhibits a high degree of fastness to light and good fastness to water, to washing and to rubbing.

#### Example 6:

By proceeding as described in Example 5 but using, instead of a woven cotton fabric, a woven fabric consisting of a 50% cotton/50% polyester fibre blend, there is likewise obtained an orange dyeing that exhibits a high degree of levelness and good allround fastness properties.

#### Example 7:

By proceeding as described in Example 1, and using the following formulation for the pretreatment (Step a)):

24 g/l of acrylate thickener (ALCOPRINT® PTF),  
100 g/l of acrylate binder (ALCOPRINT® PB-HC),  
50 g/l of wash-fast softener (ULTRATEX® FSA),  
100 g/l of water-soluble polyester resin (Worlée® Pol 192),  
5 g/l of 30% ammonium hydroxide,

applying the printing paste using a screen printing stencil, and then drying the impregnated fabric for 2 minutes at 120°C, condensing the applied polymer matrix for a further 2 minutes at 180°C, and subsequently dyeing the fabric as described under b) in Example 1, there is likewise obtained an orange dyeing that exhibits a high degree of levelness and good allround fastness properties at the locations where dye has been applied using a screen printing stencil.

Examples 8 to 59:

By proceeding as described in Example 1 but using, instead of the dye of formula (4b), one of the dyes of formulae (1a), (1b), (1c), (1d), (1e), (1f), (1g), (1h), (1i), (1j), (1k), (2a), (2b), (2c), (2d), (2e), (2f), (2g), (3a), (3b), (3c), (3d), (3e), (3f), (3g), (4a), (5a), (6a), (6b), (6c), (7), (8a), (8b), (8c), (8d), (9a), (9b), (10a), (11a), (11b), (11c), (12a), (12b), (12c), (12d), (13a), (13b), (13c), (13d), (13e), (13f) and (14a), there are likewise obtained dyeings in the colour shades of the respective dyes that exhibit a high degree of levelness and good allround fastness properties.

Examples 60 to 111:

By proceeding as described in Example 2, but using instead of the dye of formula (4b) one of the dyes of formulae (1a), (1b), (1c), (1d), (1e), (1f), (1g), (1h), (1i), (1j), (1k), (2a), (2b), (2c), (2d), (2e), (2f), (2g), (3a), (3b), (3c), (3d), (3e), (3f), (3g), (4a), (5a), (6a), (6b), (6c), (7), (8a), (8b), (8c), (8d), (9a), (9b), (10a), (11a), (11b), (11c), (12a), (12b), (12c), (12d), (13a), (13b), (13c), (13d), (13e), (13f) and (14a), there are likewise obtained dyeings in the colour shades of the respective dyes that exhibit a high degree of levelness and good allround fastness properties.

Examples 112 to 163:

By proceeding as described in Example 3, but using instead of the dye of formula (4b) one of the dyes of formulae (1a), (1b), (1c), (1d), (1e), (1f), (1g), (1h), (1i), (1j), (1k), (2a), (2b), (2c), (2d), (2e), (2f), (2g), (3a), (3b), (3c), (3d), (3e), (3f), (3g), (4a), (5a), (6a), (6b), (6c), (7), (8a), (8b), (8c), (8d), (9a), (9b), (10a), (11a), (11b), (11c), (12a), (12b), (12c), (12d), (13a), (13b), (13c), (13d), (13e), (13f) and (14a), there are likewise obtained dyeings in the colour shades of the respective dyes that exhibit a high degree of levelness and good allround fastness properties.

Examples 164 to 215:

By proceeding as described in Example 4, but using instead of the dye of formula (4b) one of the dyes of formulae (1a), (1b), (1c), (1d), (1e), (1f), (1g), (1h), (1i), (1j), (1k), (2a), (2b), (2c), (2d), (2e), (2f), (2g), (3a), (3b), (3c), (3d), (3e), (3f), (3g), (4a), (5a), (6a), (6b), (6c), (7), (8a), (8b), (8c), (8d), (9a), (9b), (10a), (11a), (11b), (11c), (12a), (12b), (12c), (12d), (13a), (13b), (13c), (13d), (13e), (13f) and (14a), there are likewise obtained dyeings in the colour shades

of the respective dyes that exhibit a high degree of levelness and good allround fastness properties.

Examples 216 to 267:

By proceeding as described in Example 5, but using instead of the dye of formula (4b) one of the dyes of formulae (1a), (1b), (1c), (1d), (1e), (1f), (1g), (1h), (1i), (1j), (1k), (2a), (2b), (2c), (2d), (2e), (2f), (2g), (3a), (3b), (3c), (3d), (3e), (3f), (3g), (4a), (4b), (5a), (6a), (6b), (6c), (7), (8a), (8b), (8c), (8d), (9a), (9b), (10a), (11a), (11b), (11c), (12b), (12c), (12d), (13a), (13b), (13c), (13d), (13e), (13f) and (14a), there are likewise obtained dyeings in the colour shades of the respective dyes that exhibit a high degree of levelness and good allround fastness properties.

Examples 268 to 319:

By proceeding as described in Example 6, but using instead of the dye of formula (4b) one of the dyes of formulae (1a), (1b), (1c), (1d), (1e), (1f), (1g), (1h), (1i), (1j), (1k), (2a), (2b), (2c), (2d), (2e), (2f), (2g), (3a), (3b), (3c), (3d), (3e), (3f), (3g), (4a), (4b), (5a), (6a), (6b), (6c), (7), (8a), (8b), (8c), (8d), (9a), (9b), (10a), (11a), (11b), (11c), (12b), (12c), (12d), (13a), (13b), (13c), (13d), (13e), (13f) and (14a), there are likewise obtained dyeings in the colour shades of the respective dyes that exhibit a high degree of levelness and good allround fastness properties.

Examples 320 to 371:

By proceeding as described in Example 7, but using instead of the dye of formula (4b) one of the dyes of formulae (1a), (1b), (1c), (1d), (1e), (1f), (1g), (1h), (1i), (1j), (1k), (2a), (2b), (2c), (2d), (2e), (2f), (2g), (3a), (3b), (3c), (3d), (3e), (3f), (3g), (4a), (5a), (6a), (6b), (6c), (7), (8a), (8b), (8c), (8d), (9a), (9b), (10a), (11a), (11b), (11c), (12a), (12b), (12c), (12d), (13a), (13b), (13c), (13d), (13e), (13f) and (14a), there are likewise obtained dyeings in the colour shades of the respective dyes that exhibit a high degree of levelness and good allround fastness properties.